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Electroless Deposition of thick Nickel-Phosphor-Dispersion Coatings

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ABSTRACT

For the chemical deposition of Nickel and Nickel-Phosphor-dispersion coatings in microstructures with various aspect ratios, a new palladium activator was investigated.

Using it, an autocatalytic directed growth of the coatings between the non-conductive and not activated walls and starting from a metallic initial layer (i.e. the ground of a structured printed circuit board) can be performed. The direction of the growth is similar to the one of the electric field.

The addition of TiO_2-particles leads to a catalytic acceleration of the Ni-P-deposition across the complete coating thickness [2]. The selective effect of the activator is predestinated fort he microstructures, because here metallic as well as non-metallic resists can be found side by side. Based upon the catalytic function of the particles, a possibility fort he deposition of thick Ni-P-dispersion coatings is described.

Index Terms **–** electrochemical deposition, microstructures, Ni-P, Ni-P-dispersion coatings, SiO_2-, Al_2O_3- TiO_2 nano particles.

1. INTRODUCTION

The investigations in [1] on the fabrication of Ni-P- and Ni-P-dispersion coatings on copper substrates have demonstrated the excellent functionality of a new generation of activation solutions based upon sulfur containing palladium complex ions. Hence, this technology has been increasingly used for the fabrication of printed circuit boards as well as for the filling of microstructures.
Similar to copper substrates, the activity of this activator was verified also for other metallic substrates (aluminum, iron, titanium, nickel) [2].
So, in microstructures with various aspect ratios an active metallic initial layer can be produced an a directed growth of the chemically deposited metal coating (Ni-P-dispersion coating) inside the structure can be achieved.

Because the non-conductive side walls of the used resists are not activated, a directed growth of the metal following the direction of the electric field achieves. Using the new ion activator, a selective activation of conductive substrate layers becomes possible and a growth of the non-conductive side walls is eliminated.

2. EXPERIMENTAL SETUP

The investigations were performed in a light sensitive lacquer structure on copper laminated printed circuit board material with 2x2 mm lateral dimensions and a depth of 40-60 µm (initial layer: copper, Fig. 1).

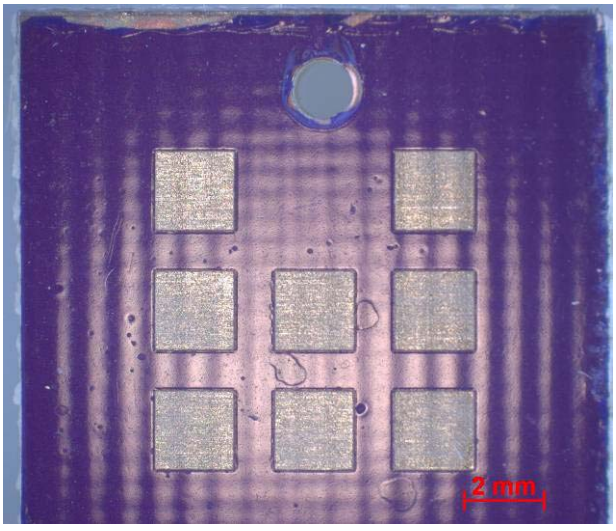


Fig. 1: Photo lacquer substrate (printed circuit board) for the deposition

The electrochemical deposition of Ni-P-coatings was performed using an acid electrolyte [2] with pH 4,6-4,8 at 82 °C an with various deposition times. The basic components of the electrolyte are $NiSO_4$ and NaH_2PO_2 (sodium hypophosphite) with additions of complex forming agents, buffers and stabilizers.
An magnetic stirrer and the blow in of air was used to avoid the settling-out of the dispersoides (TiO_2-, Al_2O_3-, SiO_2-nano particles).
The growth of the coating thickness was investigated using X-ray fluorescence and cross sections.

For the investigation of structural modifications caused by the addition of dispersoides a REM T200 SEM (manufacturer: Jeol Tokyo) was available. The allocation of the particles and formed agglomerates respectively in the Ni-P-coating was determined using a quantitative micro probe X-ray analysis [3].

3. RESULTS AND DISCUSSION

3.1. Convective flow in the dispersion electrolyte

Because the resulting flow of the dispersion electrolyte after a exposition time that depends on the particles an the concentration, leads to a spontaneous decomposition of the electrolyte, with the magnetic stirrer no higher coating thickness was achievable.
Therefore the blow in of air became necessary to investigate the catalytic effect of the particles on the deposition velocity. So a stability along more than 7 hrs exposition time became possible and all the following deposition experiments were performed using air stirring..

3.2. Particle additions

A comparison of various particle additions shows, that Al_2O_3 as well as TiO_2 particles are leading to an acceleration of the growth rate, against what SiO_2-containing electrolytes only 25 % of the coating thickness were achieved. This means, that SiO2 constricts the growth of the coating thickness (see Tab. 1)

Tab. 1: Growing rate depending on the particle material

Deposition time 1 hr	Thickn. µm	Dispersoide cont. (%)
NiP-Elektrolyte	11,8	-
NiP + 2,5 g/l TiO_2	16,7	1,12
NiP + 2,5 g/l SiO_2	4,5	1,01
NiP + 2,5 g/l Al_2O_3	17,5	1,95

The differences in the coating thickness are shown in Fig. 2 and 3.

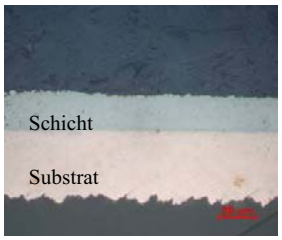


Fig. b. 2: Ni-P-Elektrolyte 2,5 g/l Al_2O_3 t_{ex} = 60 min

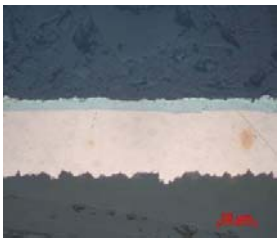


Fig. 3: Ni-P-Elektrolyte 2,5 g/l SiO_2 t_{ex} = 60 min

Because the Al_2O_3- and SiO_2 particles are worse wettable and the effect of TiO2-particles was similar to the one of Al_2O_3, only TiO_2 particle additions were used for further experiments

For the use of chemical Ni-P-coatings in structures of the micro system engineering with relocated electrodes, depending on the aspect ratio a high deposition thickness that is equal to the height of the resist is necessary

The investigations were performed using the standard electrolyte for the Ni-P-deposition with addition of 2,5 g/l TiO_2-particles.

Even though a higher particle concentration also effects a higher assembly rate of the particles, an addition of 2,5 g/l were selected, because higher concentrations easily can lead to a decomposition of the electrolyte. (see Tab. 2).

Tab. 2: Composition of the coatings depending on the concentration of TiO_2-particls in the electrolyte

Concentration of TiO_2, g/l in the electrolyte	Ti-content in the coating (%)	Ni-content in the coating (%)	P-content in the coating (%)
0,5	0	91,99	8,01
1,0	1,14	90,83	8,04
2,5	1,42	91,38	7,42
5,0	1,96	89,43	8,58
10,0	2,03	89,51	8,44

Using the selected electrolyte, coatings with a thickness up to 110 µm were deposited on lacquer structures printed circuit boards (see Fig. 1).
The acceleration of the deposition rate, measured during the first hour of 20 % (TiO_2 addition, see Fig. 6b) was efficient during the complete exposition time (max. 7 hrs, Tab. 3) and showed an nearly linear characteristic. (Fig. 4)

Tab. 3: growing rate as a function of the exposition time

Deposition time	Coating thickness	Ti-content
1 h	16,7 µm	1,42 %
4 h	55,9 µm	1,82 %
7 h	116,9 µm	2,21 %

Caused by the catalytic effect, the assembly rate of the TiO_2 increases linear with the growing rate (Fig. 4), also described for a coating thickness up to 25 µm in [2]

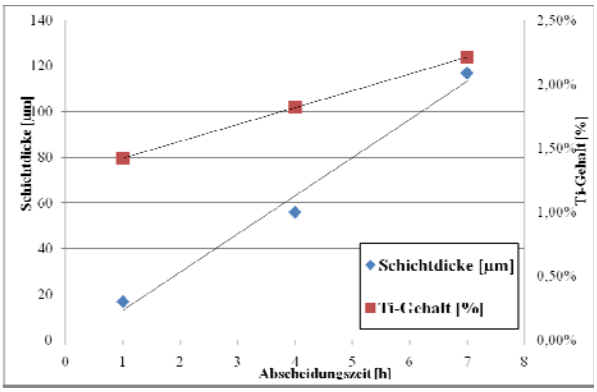
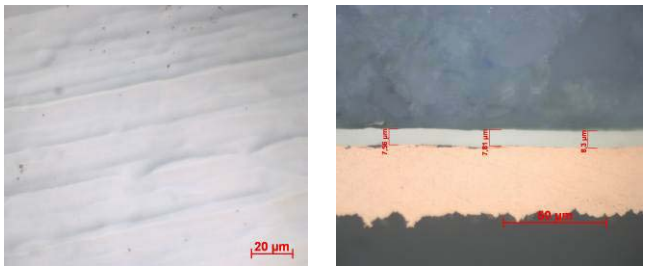


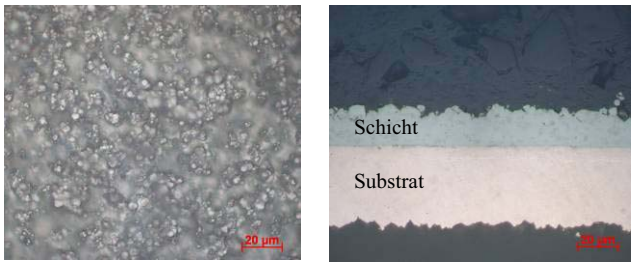
Fig. 4: Deposition rate and particle content as a function of the exposition time

In Fig. 5 and 6 the surface and coating thickness of the Ni-P-coatings with and without TiO_2 addition is shown. The coating thickness as well as the roughness of the surface are strongly increasing with the TiO_2 addition.



5a *5b*

Fig. 5. 5: Surface (5a) and coating thickness (5b) of the Ni-P-coating without TiO_2 addition, t_{ex} = 30 min



6a *6b*

Fig. 6: Surface (6a), coating thickness and roughness (5b) of the Ni-P-coating with TiO_2 addition, t_{ex} = 60 min

3.3 Comparison of the activation

Because the up to now commonly used colloidal activation solution with Pd complexes is similarly activating conductive as well as non-conductive surfaces , using such an activator the growth of the coatings also starts on the non-conductive walls of the resist (Fig. 7 and Fig. 8). The growth on the side walls is clearly visible.

Fig. 7: Ni-P-coating on the resists side wall of the structure (colloidal activator)

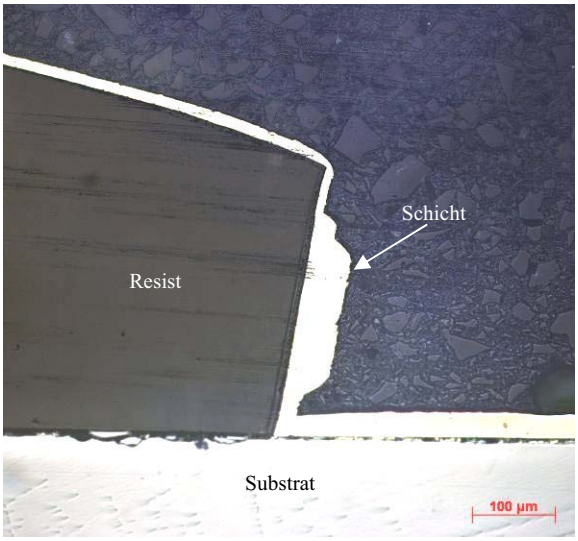


Fig. 8: Ni-P-coating on the resist wall of the structure

During the electroless deposition in structured micro systems the metallic galvanic initial layer and the structure forming resist materials are strongly connected. That's why predominantly the non-conductive resists will be affected by the activator.

In contrast, the use of ional Pd-activators shows a selective activation primarily of the metallic galvanic initial layer, supported by cementation processes.
The auto catalytic process of coating growth occurs shielded by the non-conductive not activated side walls only in one direction that is similar to the one of the electric field. After the complete filling of the structure also during the chemical deposition an overgrown of the structure occurs (Fig. 9).

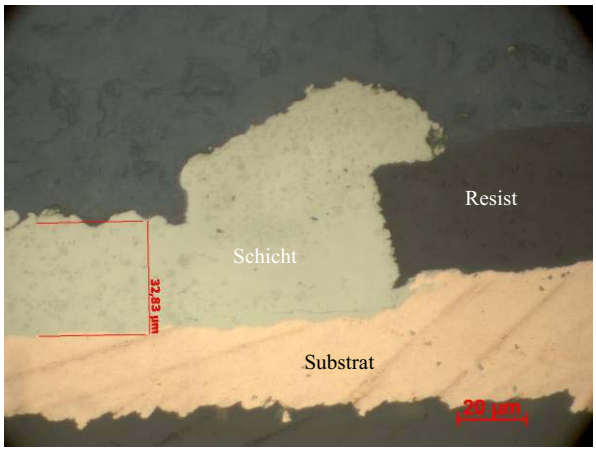


Fig. 9: Cross section of the boundary area Ni-P with 2,5 g/l TiO_2 air stirring, t_{ex} = 120 min

At higher aspect ratios, it means higher resist structures, coatings wit a thickness up to 110 µm were deposited. This let await a filling also of much lower structures independent from the substrate properties.
In contrast to the galvanic filling of various structures on a wafer, the influence of the electric field´s distribution escapes during the electrochemical deposition process. This influence often also depends on the lateral dimensions of the structures at similar depth values and leads to irregular filling degrees of the single geometries.

4. SUMMARY AND CONCLUSIONS

It was the aim of the present investigation to fill microstructure with high aspect ratios, i.e. for higher values of the coating thickness.
It is known from former works, that an addition of TiO_2 particles most effective accelerates the autocatalytic growth of Ni-P-coatings.

For the deposition of thick coatings, the coating growth on non-conductive, not activated resist walls has to be avoided to prevent the formation of pores.

Therefore an ion activator based upon Pd was used, that allows the selective activation of the relocated metallic initial layer on the ground of the structure.
The growth auto catalytically occurs from the ground of the structure only in one direction.
As a model system a printed circuit board, structured with a photo resist, a common Ni-P-electrolyte with 2,5 g/l TiO2 particle content and a Pd ion activator for the coating of the structures were used. The growing rate is constant and was fond to be 15 µm/h.

The assembly of particles in the coating increases with the exposition time and leads to an increased roughness of the coating surface.
A growth of the coating on the resist walls was almost excluded. Hence, Ni-P-TiO_2-dispersion coatings in structures with high aspect ratios can be electroless deposited.

Particularly the influence of an adverse field distribution, known from the galvanic coating of various structured wafer can be avoided.
The assembly of particle agglomerates influences the coating properties that are necessary also for specific features in micro structures.

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